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Hypothetical Deflagration of P10 from the STAR TPC: Maximum Plausible Effect

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Introduction

Under normal operating conditions, the STAR TPC holds 50 m^3 of P10 (90% argon, 10% methane) mixed from pure gases. P10 is not normally considered flammable, but can burn in air under certain conditions. Since the volume of P10 in the TPC represents considerable stored energy within a relatively thin shell, one can imagine an accident in which the gas is released. We will consider the impact of its deflagration in a worst plausible case accident: 50 m^3 of P10 stoichiometrically pre-mixed with air and ignited at the center of the gas cloud, perhaps by a spark.

Numerous interlocks make it implausible that this same volume of pure methane could be released. This scenario has been raised elsewhere, but will be considered here only for comparison.

P10 and Methane Properties

Complete combustion of methane goes as

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$$

with an energy release of 191.759 Kcal/mol (8.016 $\times 10^5$ J/mol) for gaseous products. [CERN Gas Safety Manual] The reaction doesn't change the number of gas molecules, so the expanded volume of the combustion products is due to the temperature increase. Drawing from Tables 1 and 2, the stoichiometric ratio is 9.48% to 90.52% for methane:air and 51.15% to 48.85% for P10:air.

Flammability is usually discussed in terms of "flammability range" or Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL). Values for methane and P10, from various sources, appear in Table 3. Real flammability limits, as discussed in Appendix A, are more complex: it is not as simple as P10 being flammable, while P9 is not, for example. Real limits depend on ignition energy, initial pressure and temperature, configuration and so on. Further, legally defined flammability is not equivalent to a gas being able to burn in air. Indeed, under the U.S. Dept. of Transportation classification scheme, P10 and P9 are both non-flammable.

Component	Molecular Weight	Fraction (%v/v)	Content at 20C (mol/m^3)
N_2	28.02	78.08	32.46
O_2	32.00	20.95	8.71
Ar	39.95	0.93	0.39
CO_2	44.01	0.04	0.02

Table 1: Nominal composition of air.

Component	Molecular Weight	Methane		P10	
		Fraction (%v/v)	Content at 20C (mol/m^3)	Fraction (%v/v)	Content at 20C (mol/m^3)
CH_4	16.04	100.0	41.57	10.0	4.16
Ar	39.95	0.0	0.00	90.0	37.41

Table 2: Methane and P10 composition.

Gas	LEL (%v/v)	UEL (%v/v)	Reference
Methane	5.3	14.0	Mark's Handbook, 7th Ed.
Methane	4.6	14.2	Bartknecht, 1981
Methane	4.4	16.9	CERN Gas Safety Manual
P10	44.0	54.0	Behrsing, 1981

Table 3: Flammability limits for P10 and methane from several sources.

Some general properties of methane and P10 are summarized in Table 4, including their classification under the various systems discussed in Appendix A. The representative gases listed in Table 5 give a qualitative idea as to their meaning. In all cases, methane is in the safest class.

Property	Methane	P10
Molecular weight	16.04	
LEL (%v/v)	4.6	44
UEL (%v/v)	14.2	54
Autoignition temperature	537 C	
Explosion group	IIA	
Temperature class	T1	
Density at 20 C (g/m^3)	667.	1561.
Density relative to air	0.553	1.296

Table 4: Summary of methane and P10 properties.

Gas	LEL (%v/v)	UEL (%v/v)	F Number	North America			Europe
				Flammable? (U.S. DOT)	Class	Temp.	Class
Acetylene	2.5	80	0.82	Yes	IA	T2	IIC
Hydrogen	4	76	0.77	Yes	IB	T1	IIC
Ethylene	3.1	32	0.69	Yes	IC	T2	IIB
Propane	2.2	9.5	0.52	Yes	ID	T1	IIA
Ethane	3.5	15.1	0.52	Yes		T1	IIA
Methane	4.4	16.9	0.49	Yes	ID	T1	IIA
Ammonia	16	27	0.23	No			
P10	44	54	0.10	No			

Table 5: Classification of some representative gases.

Laminar Burning

Combustion processes are discussed in Appendix B. The slowest is laminar combustion, in which the propagation velocity of a flame front through a methane-air mixture peaks at 0.4 m/s for ~9.8% methane and drops by half at 6.6% and 13.0%. For P10, the argon content significantly inerts the methane, reducing the laminar flame velocity by half—~19 cm/s, based on [Zhu, 1988].

Laminar flame temperatures, relative to the initial temperature of the reactants, are largely determined by the reaction energy and the heat capacity of the gas after combustion. For methane, this is 2238 K. For P10, interpolating measurements (from [Zhu, 1988], for example) or using the C_p values of the reaction products both give the relatively cool flame temperature of 1700 K.

Deflagration

In a typical accident environment, turbulance accelerates global flame propagation, producing deflagration. In the following description [Swenson] of methane-air deflagration in a loosely controlled environment, the flame front velocity is increased by a factor of 7 or 8:

> ...we performed open air tests to ensure we could ignite the air/methane mixture. The mixture was contained in a weather balloon, which was inflated in the tanks for the dynamic tests. This shows a night test of a balloon with an initial diameter of 5.4 feet. This is about 1/3 second after ignition, so the apparent flame speed was about 10 feet/sec. No bang, just a whoosh and strong feeling of heat.

A shock wave is, indeed, not expected for a flame velocity only 1% of the speed of sound. The maximum overpressure of a spherical flame front is $P_{max} = (7.8 \times 10^{-4}\ \mathrm{PSI})[v/(\mathrm{ms}^{-1})]^{1.72}$, based on a parameterization of Fig. 5.5 in [Bjerketvedt]. A $v = 10$ ft/s $= 3.05$ m/s flame velocity, then, yields only a 0.005 PSI overpressure, an order of magnitude below that required to break glass windows. To estimate the practical flame velocity in P10, one can scale the 10 ft/s estimate from [Swenson] by the ratio of the laminar flame front velocities (19/40) to get 1.4 m/s. However, none of the conclusions of our analysis are sensitive to this.

In general, a high density of obstacles in and around the gas cloud tends to increase turbulance and accelerate combustion, but, in the case of the STAR TPC, there's no reason to expect both premixing of a large methane-air volume and enough turbulance to drive the pressure up by the three orders of magnitude needed to approach the speed of sound.

We can infer that, unless confined, burning would occur at nearly constant pressure, not at constant volume, as in most laboratory combustion measurements. This slowly rising overpressure ("no bang, just a whoosh") scenario is seen in accidents resulting from natural and LP gas leaks; see, for example [Polytechnic].

Detonation

Flammable mixtures can be characterized by a detonation cell size; detonation generally cannot occur unless a system is large in comparison to the cell size. Some representative values, taken from plots in [Bjerketvedt], are listed in Table 6.

Studies of 1-D methane-air systems find detonation limits of 8% (lean) and 14.5% (rich). [Wolanski, 1981] The critical energy density to initiate the detonation wave is 9.42×10^{6} J/m^2, nearly flat for methane-air mixtures from 9.5–13.0%, and rising by ~60% near the detonation limits. In three dimensions, this corresponds to a critical explosion radius of $R_c = 63.4$ m and an energy of 4.76×10^{10} J. Being equivalent to the detonation of 11.4 tons of TNT, this could not occur accidentally.

A stoichiometric P10-air mix (51% P10 or 5.1% methane) can be viewed as a stoichiometric methane-air mix nearly inerted by adding 46% argon; it's clearly harder to detonate than is methane alone. A loose upper limit comes from imagining the replacement of the argon with air of equivalent

Gas	F Number	Minimum Cell Size $S_{\min}$ (cm.)	Gas Mixture (%v/v)				
			at $S_{\min}$	at $10 S_{\min}$ (upper)	at $10 S_{\min}$ (lower)	LEL	UEL
Acetylene	0.82	0.4	11	4	22	2.5	80
Hydrogen	0.77	1.5	28	17	57	4	76
Ethylene	0.69	2.5	7	4	15	3.1	32
Propane	0.52	5.0	4	2.5	7	2.2	9.5
Methane	0.49	40.0	10	?	?	4.4	16.9

Table 6: Detonation cell size for representative gases; note sensitivity to gas mixture. Values are from plots in [Bjerketvedt].

heat capacity. This gives a 7% methane-air mixture, which is below the detonation limit. In any case, the explosion radius and initiation requirements preclude an accidental detonation in any credible gas cloud leaked from the STAR detector.

P10 Combustion Scenario

Consider the combustion of a volume $V_i = (50/0.51)\ \mathrm{m}^3 = 97.1\ \mathrm{m}^3$ of stoichiometric P10-air mixture; the 208 mols of methane yield $Q = 3.987 \times 10^7$ cal $= 1.65 \times 10^8$ J of heat. We assume a 1700 K flame temperature and 1.4 m/s effective flame velocity.

The overpressure just at the end of combustion is determined by the temperature of the combustion products, and by the ratio of the initial volume of gas to the confinement volume. This approach finds a 20% lower overpressure than one gets from using the released energy and heat capacity of the room air at constant volume, i.e. by assuming that the entire released energy heats the room air uniformly. This is because of the relatively high heat capacity of the combustion products at elevated temperatures. However, as discussed later, considerable radiant heat is released, and more than 20% of the heat probably heats the walls and equipment instead of the air. In addition, real buildings are not perfectly sealed and gas would escape on the time scale of temperature equilibration.

If we assume that the gas is not confined so tightly as to alter the flame temperature, we can use the conditions

$$V_f = V_i \frac{T_f}{T_i} \cdot \frac{P_i}{P_f} \text{ and } P_f = P_i \frac{V_H - V_i}{V_H - V_f}$$

to derive the combustion volume and overpressure:

$$V_f = V_i \frac{T_f}{T_i} \left[1 + \frac{V_i}{V_H} \left(\frac{T_f}{T_i} - 1 \right) \right]^{-1} \text{ and } \Delta P = P_f - P_i = P_i \frac{V_i}{V_H} \left(\frac{T_f}{T_i} - 1 \right) .$$

We find:

$$V_f = \frac{569\ \mathrm{m}^3}{1 + 4.80 V_i / V_H} \text{ and } \Delta P = (69.6\ \mathrm{PSI}) \frac{V_i}{V_H} .$$

The volumes of the Interaction Hall and combined Interaction/Assembly Halls given in Table 7 yield the results in Table 8. R_f would be the radius of the combustion gas volume, if it were spherical. Note that the overpressures are small and only slightly affect the volumes. Combustion times are of the order

$$t_f = R_f/v_f = \frac{5.1\ \mathrm{m}}{1.4\ \mathrm{m/s}} = 3.6\ \mathrm{s}\ .$$

	Length (m)	Width (m)	Height (m)	Volume (m^3)
Interaction Hall	16	32	11.6	5,900
Assembly Hall	31	18	18.	10,000
Combined halls				15,900

Table 7: Approximate dimensions of the STAR experimental halls (Building 1006 at RHIC).

	V_f (m^3)	R_f (m)	ΔP (PSI)
Interaction Hall	522	5.0	1.1
Combined halls	547	5.1	0.4

Table 8: Combustion volume, radius and overpressure for 50 m^3 of P10.

Overpressure Considerations

Given that P10 would combust by slow deflagration without a significant pressure wave, any damage would be due to the quasi-static overpressure confined on a time scale of seconds. With the shielding wall in place between the Interaction and Assembly Halls, the gas would expand into the volume of the Interaction Hall, up to the shielding wall, with some leakage up the RHIC tunnel and around the shielding wall. Without the shielding wall in place, the gas would expand into both the Interaction and Assembly Halls. The results appear in Table 8.

The issue of shielding wall stability against a shock wave has been raised elsewhere, so we will address this for the actual, quasi-static overpressure. Assume a uniform, rectangular solid wall of height h, width $w = 1.68$ m, length l and uniform density $\rho = 2500\ \mathrm{kg/m^3}$ under a gravitational acceleration $g = 9.8\ \mathrm{m/s^2}$. Depending on various parameters, the wall could slide or tip at one or more of the surfaces between the blocks.

Shielding Wall: Sliding

Assume all surfaces have the same frictional coefficient ϵ_{fric}, and further simplify by assuming that the wall fits *inside* the doorway; the blocks would start to slide at an overpressure

$$\Delta P_{\mathrm{slide}} = \epsilon_{\mathrm{fric}} w \rho g\ .$$

For $\epsilon_{\text{fric}} = 0.5$, $\Delta P_{\text{slide}} = 20,500\ \text{nt/m}^2 = 3.0$ PSI. It is not a function of wall height, so slippage at any tier is equally likely. Coefficients of kinetic friction are ~20% lower than those of static friction, and energy considerations do not impose significant limits, so the wall's movement, once started, would be mostly limited by the escaping gas pressure.

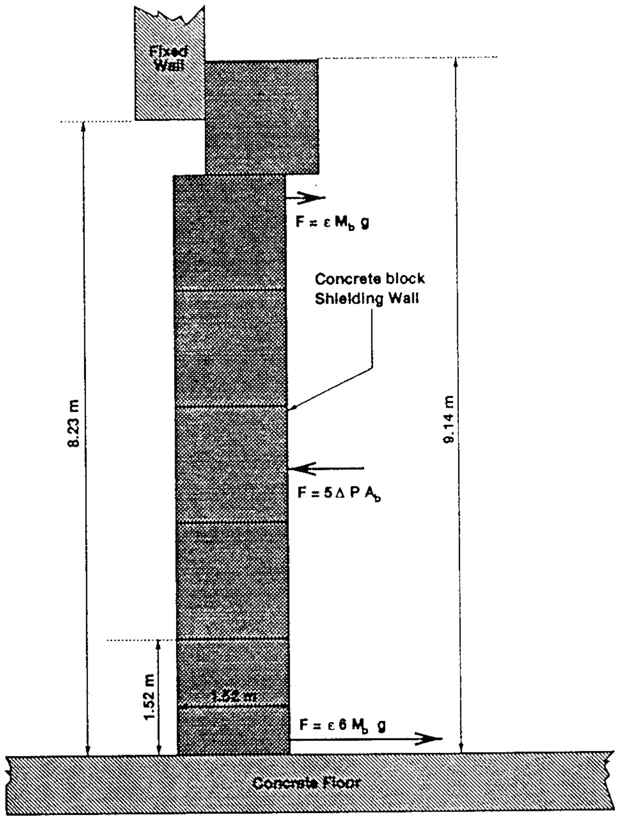

Figure 1: Shielding wall, with blocks of mass M_b stacked six high, sliding under the force of an overpressure ΔP pushing against an area A_b on each block. The upper tier of blocks is stopped by the wall above the doorway; because of its weight, the five lower tiers tend to slide as a unit.

The real wall, shown in Fig. 1, consists of $N = 6$ blocks, and the doorway is 3 ft. shorter than the wall, preventing simple translation of the wall as a whole. The top tier of blocks would strike the doorway, so that the other blocks would have to overcome friction on both their top and bottom surfaces. The minimum pressure required to translate a block is for the case of all blocks under the top tier sliding together, leaving the top tier behind. The overpressure for this is

$$\Delta P_{\text{slide}} = \epsilon_{\text{fric}} w \rho g \left(1 + \frac{2}{N-1}\right) = 28,750\ \text{nt/m}^2 = 4.2\ \text{PSI}\ ,$$

with $N = 6$ and ϵ_{fric}, ρ, w and g as before. ΔP_{slide} is considerably more than the available 1.1 PSI overpressure.

Shielding Wall: Tipping

Overpressure on the wall would also exert a torque; the wall will tip if this exceeds the restoring torques of weight and friction against the top tier of blocks. In the oversimplified case of the wall fitting inside the doorway, the minimum overpressure to tip the wall is

$$\Delta P_{\rm tip} = \frac{\rho g w^2}{h} \ .$$

Since the wall height appears in the denominator, $\Delta P_{\rm tip}$ is lower for larger heights and the wall will tend to tip from its base. Once tipping starts, the restoring torque decreases, so the wall will tend to tip until collapse. Again, energy considerations don't impose significant limits. For $h = 8.2$ m, and ρ, w and g as before, $\Delta P_{\rm tip} = 8370\ \mathrm{nt/m^2} = 1.2$ PSI.

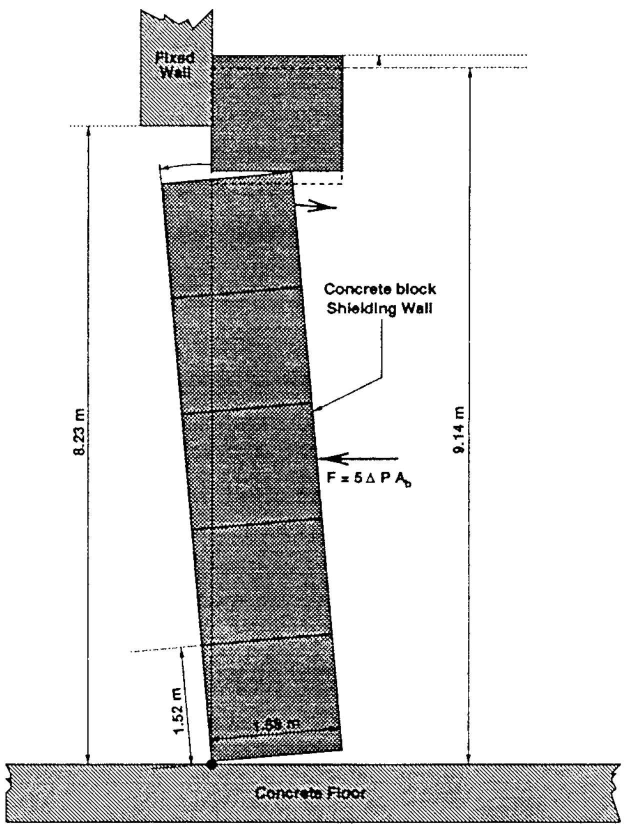

Figure 2: Shielding wall, stacked six high with blocks of mass M_b, tipping under the force exerted by an overpressure ΔP pushing against an area A_b on each block. The upper tier of blocks is stopped by the wall above the doorway; because of its weight, the five lower tiers tend to tip as a unit.

In the real case, shown in Fig. 2, the tipping wall has to slide beneath the top tier of blocks, overcoming friction and the force required to raise the top tier. The minimum overpressure to tip the wall is now

$$\Delta P_{\rm tip} = \frac{\rho g w^2}{h}\left[1 + \frac{3N-1}{(N-1)^2} + \frac{2}{N-1}\frac{h}{w}\epsilon_{\rm fric}\right] \ .$$

For $N = 6$ and the other variables as before, the correction factor is $1 + 0.68 + 1.09] = 2.77$ and $\Delta P_{\rm tip} = 3.4$ PSI. This is slightly less than $\Delta P_{\rm slide}$ but, again, considerably more than the available 1.1 PSI overpressure; the wall should be stable.

Structural Damage

Structural damage to buildings occurs at external overpressures of 0.5–2.0 PSI. As discussed in Appendix C, CERN seems to take 0.5 PSI as the safe limit for calculations involving detectors filled with flammable gas.

The Interaction Hall, consisting of 3-foot-thick reinforced concrete throughout, will not be damaged by any plausible overpressure from accidental combustion, but the Assembly Hall seems to be typical light industrial construction: curtain walls, with beams supporting a corrogated steel roof. Curtain walls are designed to withstand modest wind loading; roofs are designed to support the downward dead load of the roof's weight, plus live loads from snow, wind, workmen, etc. Neither are designed to withstand large, outward forces. The two large roll-up doors and the roof are obvious possible failure points. An overpressure of 0.4 PSI=58 PSF would subject the 6000 ft^2 roof to a total force of 350,000 pounds.

Aside from damage to the building itself, the structural damage could quite conceivably cause indirect injuries to people in, or very near, the Assembly Hall.

Thermal Radiation Considerations

In the absence of a *strong* shock wave, combustion overpressure will not cause direct injuries, but there may be burns, due to either thermal or radiant energy. Anyone within the combusting gas volume would presumably suffer thermal burns, with the severity depending, in part, on the richness of the gas mixture. (Lean natural gas explosions tend not to cause secondary fires, while rich ones do, for example. [Polytechnic]) Rapidly delivered radiant energy can also cause flash burns; for times short enough that the heat does not dissipate significantly, the thresholds are considered to be:

First degree: 2.5 $\mathrm{cal/cm^2} = 10\ \mathrm{J/cm^2}$
Second degree: 5.0 $\mathrm{cal/cm^2} = 21\ \mathrm{J/cm^2}$
Third degree: 8.0 $\mathrm{cal/cm^2} = 33\ \mathrm{J/cm^2}$

In the absence of soot and other particulates, the emissivity of the fireball is determined by its CO_2 and H_2O content. For a stochiometric P10-air mixture, the combustion product fractions are 0.464 (Ar), 0.383 (N_2), 0.051 (CO_2) and 0.102 (H_2O). A 5.1-m, expanded sphere of this mixture is optically thin, with an emissivity $\epsilon = 0.14$ at 1700 K (2600 F). Still assuming negligible cooling during combustion, the radiant power reaches:

$$P_f = 3.0 \times 10^6\ \frac{\mathrm{cal}}{s}\,.$$

A time constant of a few seconds is enough to transport heat away from the skin surface, so it should be conservative to cut off the integration of radiant heat 10 seconds after ignition. By this time, the radiated power will be a third of the maximum and about a third of the total heat will have been radiated (~13 million calories). At longer times, one cannot ignore the contraction and rising of the combustion gas; cooling through convection and conduction; and the fact that people are unlikely to remain fixed in place. Ignoring these factors tends to overestimate the flash exposures, making 2.5 cal/cm^2 radiant energy (corresponding to first-degree burns) at a distance $d = 6.5$ m from the fireball center and 4 cal/cm^2 at edge of the fireball upper limits. Serious burns should be limited almost to the combustion volume.

Comparison to Methane

A very extreme case—for purposes of comparison only—is the combustion of 50 m^3 of stoichiometrically premixed methane-air. In this case, $V_i = 50/0.0948\,\mathrm{m}^3 = 527\,\mathrm{m}^3$; ten times as much energy is released and the temperatures are significantly higher: 2080 mols of methane yield $Q = 3.987 \times 10^8$ cal $= 1.65 \times 10^9$ J of heat at a flame temperature of 2238 K (3570 F). We'll take 10 ft/s = 3 m/s as the flame front velocity. The results appear in Table 9.

	V_f (m^3)	R_f (m)	ΔP (PSI)
Interaction Hall	2530	8.4	8.6
Combined halls	3300	9.2	3.2

Table 9: Combustion volume, radius and overpressure for 50 m^3 of methane.

R_f is no longer small compared to the hall dimensions, so we cannot take it seriously, but can propagate the numbers for comparison. The combustion time is about

$$t_f = R_f/v_f = \frac{9\ \mathrm{m}}{3.\ \mathrm{m/s}} = 3\ \mathrm{s}\,.$$

Not surprisingly, the overpressure in the Interaction Hall is above that required to make the shielding wall slide and tip; it would be completely disrupted. The Assembly Hall would suffer severe damage.

For stochiometric methane-air, the combustion product fractions are 0.008 (Ar), 0.707 (N_2), 0.095 (CO_2) and 0.190 (H_2O). The emissivity will be about 0.10, somewhat lower than in the case of P10 due to the higher temperatures and optical thickness. In terms of radiated heat, the lower emissivity is much more than compensated by the T^4 factor and larger area. For either the Interaction Hall or the combined halls, the radiant power reaches

$$P_f = 1.9 \times 10^7\ \frac{\mathrm{cal}}{s}\,.$$

The methane combustion gases do not cool as quickly, and radiant energy remains important for a longer time. Following our previous estimate, one expects 2.5 cal/cm^2 radiant energy (corresponding to first-degree burns) up to a distance of mbox~ 18 m. Since the largest dimension of the Interaction Hall is 32 m, anyone there would probably suffer at least first degree flash burns. Since the combustion volume is almost half the size of the Interaction Hall, rising and turbulantly expands if the shielding wall falls and releases pressure, it is likely that anyone in the Interaction Hall could be directly exposed to the hot gas.

Conclusions

Combustion of the entire volume of P10 gas from the STAR TPC should occur by slow deflagration without a shock wave. It might, at worst, cause burn injuries to those within about 6.5 m of the center of the combustion volume, and cause structural damage to the Assembly Hall. There could be indirect injuries to those in, or near, the Assembly Hall from, for example, dislodged roofing panels. The shielding wall should not be disrupted. This relatively mild accident should not be confused with the unrealistic, but devastating, scenario in which 50 m^3 of pure methane deflagrate.

A Classification of Flammable Gases

Flammability is usually discussed in terms of the "flammability range" or Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL). Real flammability limits are more complex and depend on several factors, including ignition energy, initial pressure and initial temperature.

Ignition energy A 10 J spark is typically used for flammability testing, but accidental ignition sources need not follow this convention. Smaller ignition energies can fail to ignite a nominially explosive mixture, while larger energies expand the explosive range. This occurs because the expanding volume of the initial combustion region tends to stretch and quench the flame; a larger, hotter ignition volume is less affected. Table 10 illustrates the effect.

Ignition Energy (Joules)	LEL (%v/v)	UEL (%v/v)
1	4.9	13.8
10	4.6	14.2
100	4.25	15.1
10,000	3.6	17.5

Table 10: Effect of ignition energy on methane flammability (Bartknecht, 1981, quoting H.Christner).

Initial Pressure Flammability limits are usually quoted at one atmosphere pressure; higher initial pressures tend to expand the explosive range, raising the UEL, especially. However, the pressures involved with the STAR TPC should not deviate far from this.

Initial Temperature Flammability limits are also usually quoted at room temperature. Not surprisingly, since flammability is mostly a matter of released energy and heat capacity, such that the temperature of unburned gas at the flame front is raised enough to allow a high reaction rate, higher initial temperatures expand the explosive range. Extrapolating, the LEL for methane drops to zero by about 1400 C. In other words, molecular energies are then high enough that methane oxidises spontaneously, without requiring further heating at the flame front.

This effect is shown graphically in Fig. 4.2 of [Bjerketvedt]. As one would expect, the autoignition temperature (temperature required to ignite a stoichiometric mixture) is well below that required to drive the LEL to zero. For methane-air, the autoignition temperature is 537 C. However, the temperatures involved with the STAR TPC are all close to room temperature.

Flammability Definition: U.S. Dept. of Transportation

The U.S. Department of Transportation, (DOT, Flammable Liquids and Gases) classifies gases according to flammable range. A gas is said to be flammable if:

1. Its LEL is below 13% in air; or

2. It has a flammable range greater than 12%, regardless of its LEL.

Under this system, it's quite possible for a gas to burn in air, and yet be classified as non-flammable. Usually, it will be classified simply as a compressed gas. Ammonia is an example: its LEL=16% and UEL=27%, making it legally non-flammable. Yet, it causes severe damage when a large volume ignites in a confined space.

F Number

"F number," defined as $F = 1 - \sqrt{(\mathrm{LEL})/(\mathrm{UEL})}$, is a recently proposed [Kondo, 1994] measure of gas explosion hazards. The authors argue that:

> It has several advantages over conventional explosion hazard indices. Its value ranges from 0 to 1, which is convenient to compare the relative properties of different materials... classification of various gases according to the degree of hazard can be made automatically by using this value...

North American Gas Classification

In the U.S. and Canada, hazardous materials are classed according to type: [Hydrobond]

Class I: Flammable gases and vapours.

Class II: Combustible dusts.

Class III: Flyings (Cotton linters, Sawdust etc).

These classes are then sub-divided into groups A–D. For gases (Class 1) the groups are are given in Table 11. Gases are also classified according to ignition temperature, as in Table 12.

Class	Representative Gas
A	Acetylene
B	Hydrogen
C	Ethylene
D	Propane / Methane

Table 11: North American gas classification scheme.

North American Temperature Class	European IEC/CENELEC Maximum Surface Temperature (degrees C)
T1	450
T2	300
T3	200
T4	135
T5	100
T6	85

Table 12: North American and European gas classification by ignition temperature.

European Gas Classification

In European practice, gases are grouped by the amount of energy required to ignite its most explosive mixture with air. CENELEC/IEC gas groupings are divided: Group I for Mining and Group II for surface industrial applications. Group II is further sub-divided into IIA, IIB and IIC, as in Table 13.

Gas Group	Representative Gas	Temp. Class	Ignition Energy (microjoules)
IIA	Methane	T1	280
IIA	Propane	T1	260
IIA	Ethane	T1	260
IIB	Ethylene	T2	95
IIC	Hydrogen	T1	18
IIC	Acetylene	T2	20

Table 13: CENELEC/IEC gas classification by minimum ignition energy for any fuel-air mixture.

The minimum ignition energy does not necessarily occur for the stoichiometric fuel-air mix, but tends to be close to it. For fuel-air mixtures a factor of two on either side of the minimum, the ignition energy is usually a factor of 2–3 higher. The ignition energy is also a strong function of experimental conditions (rate of discharge, electrode geometry, etc.) and should not be taken too literally.

Mining Standards

One can reasonably take 1% methane in the air as a safe, practical level, since U.S. law (United States Code, Title 30, Chapter 22, Section 873) states, with regard to mining safety, that:

> ...tests for methane shall be made immediately before such shots are fired and if 1.0 volume per centum or more of methane is present, when tested, such shot shall not be made until the methane content is reduced below 1.0 volume per centum.

By these standards, one would be limited to 10% P10 in a room, (by which point O2 displacement would also be of interest). P10 density has 1.30 times the density of air at 20 C. In considering any density effect due to the argon, one should note that CO_2, known to "pool" only in extremely still air, is 1.26 times as dense.

B Combustion Processes

Laminar Flame Velocity

Quoting from [Bjerketvedt]:

> When the cloud is ignited by a weak ignition source (i.e. a spark or a hot surface) the flame starts as a laminar flame. For a laminar flame the basic mechanism of propagation is molecular diffusion of heat and mass. ...This diffusion process of heat and mass into the unburned gas is relatively slow and the laminar flame will propagate with a velocity of the order of 3-4 m/s.

(As discussed in the main text, laminar flame velocities are an order of magnitude lower in methane-air mixtures, and even lower in P10-air mixtures.)

Transition to Deflagration

Laminar flame propagation dominates in some tightly controlled environments (e.g., a Bunsen burner), but accident environments are seldom so simple; the hot, burned gases usually disturb the unburned gas volume significantly, creating a larger, turbulent flame surface. The global flame propagation can be significantly faster, if the length scale of the turbulance exceeds the flame front thickness. Turbulent burning is termed "deflagration."

Detonation

A succinct description of a detonation appears in [Bjerketvedt]:

> A detonation is the most devastating form of gas explosion. Unlike the deflagration, a detonation does not require confinement or obstructions in order to propagate at high velocity. Particularly in an unconfined situation, the behaviour of a detonation is quite different from a deflagration. A detonation is defined as a supersonic combustion

wave (i.e. the detonation front propagates into unburned gas at a velocity higher than the speed of sound in front of the wave). The gas ahead of a detonation is therefore undisturbed by the detonation wave. In fuel-air mixtures at atmospheric pressure, the detonation velocity is typically 1500 - 2000 m/s and the peak pressure is 15-20 bar.

[Bjerketvedt] continues, saying:

> The probability of occurrence of a detonation in fuel-air mixtures depends strongly upon the type of fuel. Very reactive fuels, such as hydrogen, acetylene or ethylene, may detonate in an accident situation. For accident situations involving such fuels, detonations should be regarded as a possible scenario.
>
> Other fuels are less likely to detonate. In particular no data exist on detonations involving pure methane-air. Generally, however, in large gas clouds with a high degree of confinement and/or with a high density of obstructions, detonations cannot be ruled out.

However, in the cases of P10 or methane, one can be much more quantitative than this, as was discussed in the main text. Moderate volumes of P10 or methane are almost impossible to detonate in an open cloud. Even large volumes require enormous ignition energies, of the order of tons of TNT equivalent.

C Risk Classification of Flammable Gases (CERN)

One method of classifying the accident potential of systems is by their stored energy; CERN, for example, groups systems into four Risk Classes, scaling the quantity of gas by their heat of combustion, relative to hydrogen (57.798 Kcal/mol or 28,900 Kcal/kg). [CERN Gas Safety Guide 35.1.10] Physically separated areas can be treated individually. The safety guide goes on to qualify

Risk Class	Q_{tot} Range: H_2 Equiv. (kg)	Volume Range: CH_4 Equiv. (m^3 at 1 Bar, 20 C)	Description
0	0	0	Risk of a small local flash fire
1	< 0.4	< 1.45	Risk of a local fire in a single set-up
2	$0.4 \rightarrow 40$	$1.45 \rightarrow 145$	Risk of general fire, involving other set-ups
3	> 40	> 145	Risk of explosion

Table 14: CERN risk classifications for flammable gases).

these risk classifications; to summarize:

1. Dilution with inert gas is, however, always a step towards safety, not only because the range of flammability narrows but also because the speed of potential combustion reactions is reduced by the diluent. This reduces the explosion hazard and should be taken into account.

2. The confinement criterion, relating the risk of an explosion (pressure build-up after deflagration) to the volume of the building surrounding the flammable gas container(s), or more precisely, the smallest practically enclosed space with solid walls around it.

   Explosive pressure could occur if the amount of escaped flammable gas inside the confined volume filled more than 0.5% of it with an explosive gas/air mixture at the moment of ignition. The following formula gives an estimate of the minimum volume required of a lab room (with solid walls) to avoid explosive pressures in case of ignition:

$$V_{\mathrm{LAB}} = \frac{20,000 \times V_{\mathrm{esc}}}{\mathrm{LEL}}$$

   where V_{LAB} is the minimum safe volume (in m^3) of the lab and V_{esc} is the volume (in m^3 at atmospheric pressure) of the flammable part of the escaped gas that remains inside the lab in concentrations above the LEL (in percent).

3. The criterion of leak/ventilation dynamics relates gas accumulation probabilities to ventilation and to worst credible leak condition.

4. The common sense criterion is applied in the final evaluation, correcting the over-simplification introduced by the three preceding criteria.

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